0.42 in (12, 12). The values of γ obtained here suggest it is likely to be situation (ii), namely the transition from linear to the anomalous regime. The larger value of \( \gamma = 0.63 \) for Ar in (8, 8) might mean that it lies in the anomalous regime where \( D \) increases with \( \gamma \). On the other hand, the values 0.50 and 0.42 in all likelihood lie in the linear regime. The value of \( \gamma = 0.50 \) most likely corresponds to the minimum in \( D \) at the transition from linear to the anomalous regime. Thus our inference is that in the case of Ar, \( \gamma \) lies in the crossover from the linear to the anomalous regime and therefore has a non-monotonic dependence. Thus, a more convincing explanation of the self-diffusivity and its variation in nanotubes of different diameters suggest that smoothness cannot explain the trends seen, although smoothness might offer a suitable explanation for the higher diffusivities of guests in carbon nanotubes compared to zeolites.

In summary, our study demonstrates a crossover from a diffusive behaviour (with \( \alpha \approx 1 \)) at small sizes (\( \gamma < 0.5 \)) of the sorbate to superdiffusive nature (\( 1 < \alpha < 2 \)) with increase in size, eventually approaching ballistic motion when the sorbate size is similar to that of the host. The crossover has been explained quantitatively: \( \langle F^2 \rangle \) decreases with increase in the levitation parameter \( \gamma \) (eventually vanishing as \( \gamma \to 1 \); Figure 3). The superdiffusive nature is not suppressed even at higher loadings (at least up to 44% of saturation loading). Temperature variation suggested the temperature dependence of the diffusion constant to be non-Arrhenius. Flexible nanotube simulations for \( \sigma_{68} = 7 \) Å at the same temperature yield marginally lower exponent. Indeed, even at a relatively higher temperature of 400 K, we found\(^7\) \( \alpha \approx 1.68 \). More detailed simulations to understand the contributions from different factors to the observed behaviour are in progress. Finally, the line of reasoning based on the levitation parameter affords a basis for explaining the seemingly conflicting trends of Skoulidas et al.\(^4\) and Ackerman et al.\(^5\).


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Oxyboron complexes of C\(_{60}\)-fullerene: a new direction in fullerene chemistry

Rahbabal Debnath* and Rampada Sahoo

Glass Science Section, Central Glass and Ceramic Research Institute, 196 Raja S.C. Mullick Road, Kolkata 700 032, India

A series of oxyboron and (bismuth)-oxyboron addition complexes of fullerene have been synthesized by solid-state reaction between C\(_{60}\) and (a zinc, bismuth) borate glass at 650–700°C under argon atmosphere. Boron ions of different network chains of the glass were found to add to the incorporated C\(_{60}\) via oxygen-bridge, where the bismuth oxide of the glass acted as a promoter. The complexes remained encased in the matrix of the glass, imparting a green colour to the latter. The complexes attached to the relatively smaller unit of boron/bismuth-boron chains, were possible to extract out by eluting a powdered sample of the composite with toluene, and were then characterized by UV–VIS–NIR absorption, mass and IR studies. The linkages between the boron ions of different network chains and the incorporated C\(_{60}\) thus formed, were found to make the glass more stable and a better electrical conductor.

Buckminsterfullerene (C\(_{60}\)) has been proved to be much more reactive\(^{-12}\) than was originally thought. This is because the pentagonal rings adjacent to benzenoid rings of the molecule are structurally strained, and hence have a tendency to avoid double bonds leading to a poor delocalization of the electrons. As a consequence, the molecule behaves more as an electron-deficient super alkene

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*For correspondence. (e-mail: debnath@cgcri.res.in)
than as a super-aromatic. Many of its reaction products are however unstable and have the tendency to eliminate and reform the parent fullerene. Here we report the synthesis of a series of oxyboron and (bismuth, oxyboron) addition complexes of C_{60}, which show relatively better stability.

The complexes of fullerene (C_{60}) were prepared by solid-state chemical reaction between the frits of a zinc bismuth-borate glass of composition (mol%) B_{2}O_{3} = 30–45, Bi_{2}O_{3} = 20–45 and ZnO = 10–40, and fullerene (C_{60}), at a temperature of 650–700°C under inert atmosphere. All chemicals used in the preparation of the precursor glass were of GR grade (E Merck) and the C_{60} fullerene used was of 99.9 ± % (Lancaster, UK). At a temperature of 650–700°C, the mixture transformed into a homogeneous melt. The reaction was allowed to occur for 30 min and then rapidly quenched to a monolithic solid of green colour. A portion of this composite glass of desired dimension was polished and its absorption spectrum was studied.

The observed unusual change in colour as well as absorption spectrum of the glass after incorporation of fullerene, indicated that fullerene had undergone chemical interaction with some constituents of the glass. To investigate the nature of interaction precisely, we extracted the relatively smaller sized fullerene-bonded species out of the matrix as follows. A certain amount of frit of the composite was crushed to powder in a mortar under immersed condition in toluene, when a continuous flash of argon was passed through the solvent and the mixture was stirred vigorously. Toluene, in contact with the surface of the composite powder, was able to dissolve out relatively smaller sized complexes in this process. The mixture was then rapidly filtered-off to obtain a clear filtrate. Because of an observed phenomenon of slow degradation of the complexes in air, only instantly prepared such filtrates were used to study UV–VIS–NIR, mass and IR spectra of the complexes. It was, however, ascertained by recording the spectra of a number of such extracts as a function of time that within the first 4–5 min of extraction, the extent of degradation of the complexes is insignificant and the spectrum remains unaffected.

All absorption spectra were studied in a Shimadzu UV–VIS–NIR Absorption Spectrometer (Model 3101, Japan). The IR spectrum of the mixture of the complexes was recorded in a Perkin Elmer FTIR spectrometer. Because of strong absorption of different vibrations of the host borate glass in the same frequency region, it was not possible to detect the IR bands of the complexes in the spectrum of the composite. The spectrum of the complexes was, therefore, recorded by depositing a thin film of the complexes on a KBr pallet using a toluene extract as described above.

The electron spray ionization (ESI) mass spectrum of the mixture of the complexes was recorded in a Micromass Quattro Mass Spectrometer (Model: LC-MS, USA) using a similar instantly extracted solution of the complexes in toluene.

A sample of the filtered extract was also subjected to qualitative chemical analysis to detect the inorganic part of the complexes. Bismuth oxychloride test with the filtrate showed presence of bismuth ions, while a methyl borate test indicated the presence of borate in the extract.

To check whether or not boron can add with C_{60} in the absence of bismuth oxide, we prepared a similar composite using a lead-borate glass and C_{60}. No unusual change of colour or absorption spectrum was noted in this case.

Figure 1 shows the absorption spectrum of the green composite along with that of the base glass. The averaged absorption spectrum of the fullerene complexes extracted from the composite by toluene and that of pristine fullerene in the same solvent are also given in Figure 1. A photograph of a sample of the composite glass is shown in the inset. The composite shows an absorption-hump around 470 nm and two relatively weak absorption bands at around 582 and 635 nm. The toluene extract of the complexes exhibits absorption bands at around 428, 540, 675 and 770 nm in the visible region and at 274 and 284 nm in the UV. The VIS absorption spectra of both the composite and the extract are found to differ from those of the base glass and the pristine fullerene, in respect of energy, intensity and absorption feature.

The host glass is an oxide glass of zinc–bismuth borate, and the composite was realized by melting the glass–C_{60} mixture at a temperature of 600–700°C under inert atmosphere. Hypothetically, under such conditions, the possible entities of the glass with which C_{60} can react are boron,
bismuth and zinc ions, trapped oxygen and water. In our earlier studies\textsuperscript{13} with a number of C\textsubscript{60}-containing (zinc, lead) phosphate glasses, we did not observe any detectable interaction of C\textsubscript{60} with zinc ions. It is also known from literatures\textsuperscript{14,15} that in case of complexes of C\textsubscript{60} with zinc porphyrin, only a weak interaction between C\textsubscript{60} and the zinc ion persists. Such weak interaction is not expected to produce a complex that could be isolated from the solid by extraction. We therefore, exclude the possibility of formation of any strong complex of C\textsubscript{60} with zinc ions. Thus possible reactions only with oxygen, water, boron and bismuth ions of the glass are considered.

It is known from literature\textsuperscript{10-12} that C\textsubscript{60} undergoes a change in its electronic and vibronic structure when it reacts with an electron donating metal or other ions through opening one of its pyracylene bonds, e.g. addition with Pt(PPh\textsubscript{3})\textsubscript{2} or Pd(PPh\textsubscript{3})\textsubscript{2}. As a consequence, its (h\textsubscript{n} \rightarrow t\textsubscript{1g}) 405 nm absorption band shows a red shift; the absorption valley at 435 nm becomes broader and red-shifted. Its symmetry-forbidden h\textsubscript{n} \rightarrow t\textsubscript{1u} (HOMO \rightarrow LUMO) transitions (\sim 600 nm) also get stronger in intensity with a red shift because of loss of symmetry of the molecule. We had earlier noted\textsuperscript{16} the above phenomenon when Br\textsuperscript{3-} ion adds with fullerene through donation of its lone pair of electrons. The (h\textsubscript{n} \rightarrow t\textsubscript{1g}) 405 nm band of C\textsubscript{60} in such a case shifts to \sim 470 nm and becomes strong in intensity; as a result its symmetry-forbidden h\textsubscript{n} \rightarrow t\textsubscript{1u} (HOMO \rightarrow LUMO) transitions get merged with the tail of the former, losing their distinct identity. Considering the energy and absorption intensity of the 470-nm hump of the present composite, we associate the band with the absorption feature of a bismuth complex of C\textsubscript{60}. One interesting feature of the spectrum of the present complexes, both in solid and solution, is that the h\textsubscript{n} \rightarrow t\textsubscript{1g} (HOMO \rightarrow LUMO) bands (e.g. the 582 and 635 nm bands in case of the composite and the 675 and 770 nm bands in case of the extract) of the C\textsubscript{60} cage are clearly discernible. An unusual red shift of these bands in the case of solution is noted. The complexes in the glass structure remain surrounded by the bismuth-borate random network chain; so apart from experiencing surrounding electrostatic field, the complexes are likely to exist in the system with strain structures. In solution, the complexes are free to attain their respective relaxed structures, which possibly shift their absorption bands to longer wavelength. A similar phenomenon was also observed\textsuperscript{18} earlier in case of bismuth-related complexes of C\textsubscript{60}, which on migration from the solid host to solution, suffer a red shift in their 470 nm band to 540 nm.

Considering the origin of the 428 nm band observed only in the case of the extract, we note that direct addition of oxygen or addition of the other major constituent of the glass, i.e. boron, with C\textsubscript{60} via oxygen-bridge may give rise\textsuperscript{5} to this band. Such a band is known in case of absorption spectrum of fullerene epoxides\textsuperscript{6} (424 nm). Chemical detection of boron in the extract of the complexes and an observed red shift of the band, however, suggest the possibility of association of the 428 nm band with an oxygen mediated chemical attachment of boron with fullerene. In case of the spectrum of the solid, the 428 nm band remains submerged by the relatively stronger 470 nm band of the bismuth addition complexes described above. As the 470 nm band of the bismuth complexes shifts to 540 nm due to migration of the complexes from solid to solution, the 428 nm band becomes discernible.

Concentrating on the UV part of the spectrum, we note that the lowest energy absorption band of the toluene itself remains restricted within 268–269 nm, and a simple pure borate or bismuth-borate species does not have\textsuperscript{17} any absorptions in the wavelength region higher than 250 nm. It is rational therefore, to believe that the observed UV absorption bands around 274–284 nm are related to the C\textsubscript{60} component of the complexes. In fact, the UV absorption bands of the mixture of complexes (e.g. 274–284 nm split band) are energetically close to those of the 272 nm dipole-allowed π → π* bands of pristine C\textsubscript{60} in toluene.

The ESI mass spectra of a mixture of fullerene complexes (extracted from the composite), in the mass range 700–3000 amu is shown in Figure 2. The spectrum shows existence of a number of species with masses higher than the mass of pristine fullerene (720 amu) in different proportions. Among all these products, only three species respectively, of masses 907 (48%), 925 (100%) and 2931 amu (34.5%) are dominant in concentration. So we limit our discussions to these three species only. Considering the fact that (zinc, bismuth) borate glass is an inorganic glass which is not soluble in toluene, it is reasonable to assume that the species which got dissolved from the glass into toluene should either be fullerene itself or its fragments or some derivatives of fullerene. Only the derivatives of fullerene can have masses above 720 amu. Again, fullerene is an organic molecule which has been incorporated in an inorganic glass; so the possibility of existence of some fraction of C\textsubscript{60} in the host, as molecular clusters cannot be ruled out.

Figure 2. Mass spectrum of boron and bismuth complexes of fullerene extracted from the green composite (G).
out. During the process of rapid quenching of the fullerene-containing molten glass from a temperature of 700/600 to 300°C, such C\textsubscript{60} clusters are expected to experience high hydrostatic pressure. At such high temperature and pressure, the fullerene molecules of the clusters are likely to undergo cycloaddition reaction with each other, forming polymerized fullerene\textsuperscript{18,19} (dimer\textsuperscript{20}, trimer\textsuperscript{21}, etc.). In fact, detection of species of mass 2163 amu in the mass spectrum confirms the formation of fullerene trimer. The observed difference between the calculated (2160 amu) and experimental mass for the C\textsubscript{60}-trimer might be due to occasional association of \textsuperscript{13}C isotopes with the fullerene cage.

In a recent laser photoionization time-of-flight mass spectral study of a bismuth-borate glass (i/B\textsubscript{2}O\textsubscript{3} : B\textsubscript{2}O\textsubscript{3}, where j = B\textsubscript{2}O\textsubscript{3}B\textsubscript{2}O\textsubscript{3}) containing high proportion of bismuth, Stenz et al.\textsuperscript{22} showed that structural units of relatively smaller masses, namely BO\textsubscript{2}, B\textsubscript{2}O\textsubscript{3}, B\textsubscript{3}O\textsubscript{5}, Bi\textsubscript{2}O\textsubscript{5}, BiB\textsubscript{2}O\textsubscript{5}, Bi\textsubscript{2}O\textsubscript{5} and Bi\textsubscript{2}O\textsubscript{6} are present in such glass along with different long bismuth-borate chains. As stated earlier, the trapped oxygen, water and boron and bismuth ions of different bismuth-borate units/chains of glass, may take part in chemical reactions with the incorporated C\textsubscript{60} forming various addition complexes. Among these fullerene complexes, the species in which fullerenes are attached to the relatively smaller inorganic units are only likely to get dissolved in toluene, while the complexes attached to longer inorganic chains will not.

The occurrence of mass 752 amu in the spectrum gives an indication that fullerene di-epoxide\textsuperscript{5} O \textsubscript{<C\textsubscript{60}>} O is formed in the composite. In fact, during the cooling cycle of the molten composite, the temperature and pressure inside remain high. Under such high temperature and pressure, the trapped oxygen of the melt may react with fullerene forming epoxide via opening of one of the pyracylene bonds of the latter, which are known to be of olefinic nature. Similar addition reaction of oxygen with olefin is well known in the case of industrial preparation of ethylene oxide. Presence of bismuth oxide in the system possibly helps the present oxidation reaction. Such mono or di-epoxides\textsuperscript{5,6} of C\textsubscript{60} of the system, actually act as a precursor in the formation of all oxyboron or (bismuth)-oxyboron complexes of C\textsubscript{60}. The detail of the reaction is as follows: A fullerene epoxide in the system is first converted to dihydroxy fullerene by the action of trace trapped water and acidic B\textsubscript{2}O\textsubscript{3} of the glass. Such dihydroxy fullerene then further reacts with different borate units of the system to yield oxy boron derivatives. The species of mass 907 amu, detected in the mass spectrum is formed by the addition reaction of a di-epoxide with BO\textsubscript{3} and B\textsubscript{2}O\textsubscript{3} unit of the glass\textsuperscript{22} via formation of a tetra hydroxy fullerene [(B\textsubscript{2}O\textsubscript{6}C\textsubscript{60}(BO\textsubscript{3}) (M = 907–908 amu, M\textsubscript{obs} = 907 amu)].

\[ \text{BO}_2 + O < C_{60} > O + B_2O_3 \rightarrow \]
\[ [O-B-O_2 \supset C_{60} \subset O_2 > B_2O_4]^-. \] \hspace{1cm} (1)

In a similar reaction, the di-epoxide may add with the B\textsubscript{2}O\textsubscript{6} and BO\textsubscript{2} fragments of glass\textsuperscript{22} forming (O\textsubscript{2}B\textsubscript{2}C\textsubscript{60} (BO\textsubscript{3}) (M = 924 amu, M\textsubscript{obs} = 925 amu) molecule. The reaction may be written as:

Reactions similar to eq. (1)

\[ \text{BO}_2 + O < C_{60} > O + B_2O_3 \rightarrow \]
\[ [O-B-O_2 \supset C_{60} \subset O_2 > B_2O_4]^-. \] \hspace{1cm} (2)

The third major species of mass M = 2932 amu, may be formed through a similar reaction when mono-epoxide of a fullerene trimer adds simultaneously with a BO\textsubscript{2} unit and two bismuth-borate units, namely BiB\textsubscript{2}O\textsubscript{6} and BiB\textsubscript{2}O\textsubscript{5} of glass\textsuperscript{22}. In our previous study\textsuperscript{16}, we showed that a bismuth-borate unit of glass adds with a fullerene moiety through donation of the lone pair of electrons of its bismuth ion to a pyracylene bond of the latter. The reaction may be written as:

Reaction eq. (1) and that described in ref. 16.

\[ O_2B_4Bi + O_2B_3Bi + [C_{60}] > O + BO_2 \rightarrow \]
\[ O_2B_4Bi + [C_{60}] \subset O_2BONa \]
\[ \cup BiB_2O_3 \] \hspace{1cm} (3)

The sodium ion of the product of eq. (3) is an adduct stencil from the chamber. The complexes are shown in Table 1.

Relative intensity distribution of the species suggests that all oxyboron complexes together form the dominant species in this composite. It is therefore, obvious that the composite itself or the toluene extract thereof, will mainly exhibit the characteristic feature of the oxyboron complexes, both in the absorption and IR spectra.

Because of the tendency of degradation of the complexes in ambient atmosphere, we could not separate the complexes individually from the mixture using normal chromatographic technique. But the results of the mass spectrum showed that the complexes in the mixture have only two types of chromophoric groups, boron-related and bismuth-related complexes. This phenomenon helped us to analyse successfully both the absorption and IR spectra of the complexes in the mixture.

The IR spectrum of the thin film of the mixture of complexes of the composite recorded in the frequency range 500–2000 cm\textsuperscript{-1} is shown in Figure 3 along with that of the base (zinc bismuth) borate glass. It is clear from the spectrum in Figure 3 a, that the base glass, i.e. the zinc bismuth-borate glass has only four distinguishable, prominent IR absorption bands at 702, 911, 1024 and 1278 cm\textsuperscript{-1} in the frequency range studied.

Vibrations of bismuth-oxygen polyhedra are normally known\textsuperscript{24} to appear at a frequency range below 450–500 cm\textsuperscript{-1}. The zinc ions of glass mainly remain in the interstitial positions. So, zinc-related phonon vibration is also not
Table 1. Formula and structure of complexes detected in the mass spectrum of the green composite

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Mass of the C_{60}-complexes detected</th>
<th>Proposed formula of the complexes</th>
<th>Proposed possible structure of the complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>907 (48%)</td>
<td>BO_{3}C_{60} B_{2}O_{6}</td>
<td>![Structure 1]</td>
</tr>
<tr>
<td>2</td>
<td>925 (100%)</td>
<td>BO_{3}C_{60} B_{2}O_{7}</td>
<td>![Structure 2]</td>
</tr>
<tr>
<td>3*</td>
<td>2931 (34.5%)</td>
<td>BiB(O_{3}) [C_{60}], BiB_{x}O_{y} BO_{z}Na</td>
<td>![Structure 3]</td>
</tr>
<tr>
<td>**</td>
<td>752 (8.6%)</td>
<td>C_{60}O_{2}</td>
<td>![Structure 4]</td>
</tr>
<tr>
<td>**</td>
<td>2163 (22%)</td>
<td>[C_{60}]</td>
<td>![Structure 5]</td>
</tr>
</tbody>
</table>

Masses and formulae of glass-fragments of bismuth-borate glass that can add with fullerene moieties are: 42-43 [(BO_{3})_{2}], 110-113 [(BiB_{x})_{2}], 179-185 [(BiB_{y})_{2}], 293-295 [(BiB_{x}O_{y})], 309-311 [(BiB(O_{3})_{2}], 336-338 [(BiB_{x}O_{y})], 378-381 [(BiB_{y})_{2}].

*Source of Na⁺ ion (one of the adduct stencils) is the ionization chamber.

**These species are included to show that fullerene epoxides which are precursors to the boron complexes and the trimers are actually formed in the glass.

expected in this frequency range. The IR bands of the base glass should, therefore, be associated with the vibrations of different borate anions of the glass. It has been already established from earlier studies\textsuperscript{25,26} that in a [xBi_{2}O_{5}-(1-x)B_{2}O_{3}] glass, the content of tetrahedral [BO_{4}] structural units increases at the cost of [BO_{3}] units with the increase in concentration of Bi_{2}O_{5} and reaches a maximum when the Bi_{2}O_{5} concentration is around x = 0.45 mol. The present glass being high bismuth-containing borate glass, it should have a large content of [BO_{4}] tetrahedron along with planar orthoborate [BO_{3}] units. The observed band at 1024 cm\textsuperscript{-1} due to asymmetric stretching ν_{as}[B_{4}O_{10}^{-}] of the BO_{4} unit, and the bands at 1278 cm\textsuperscript{-1} [ν_{as}(B_{2}O_{3})], 911 cm\textsuperscript{-1} [ν(B_{3}O_{3})] and 702 cm\textsuperscript{-1} [γ(B_{3}O_{3})] due to the BO_{3} units, do actually show that the glass contains both the BO_{4} and BO_{3} units in its structure\textsuperscript{25,27-29}.

Pristine C_{60} molecule has\textsuperscript{18,19} only four strong IR absorption bands at 526, 576, 1182 and 1428 cm\textsuperscript{-1} due to intramolecular F\textsubscript{1u} modes and a weak band at 1539 cm\textsuperscript{-1} due to the cage vibration. The spectrum of the mixture of complexes of the extract of the composites, on the other hand, shows a number of IR absorption bands. It shows relatively strong bands at 700, 740, 1035, 1070, 1130, 1270-1290, 1385, 1540 and 1740 cm\textsuperscript{-1}. A band of moderate intensity is also observed at 1460 cm\textsuperscript{-1}.

The band at 1540 cm\textsuperscript{-1}, which is associated with the C_{60} fullerene-cage vibration\textsuperscript{18,19} is known to remain unaffected even when the molecule undergoes some addition reaction. Occurrence of the 1540 cm\textsuperscript{-1} band in the spectrum therefore, definitely shows the presence of C_{60} molecules in these complexes. The IR bands at ~700 cm\textsuperscript{-1} and ~1035 cm\textsuperscript{-1} of the complexes of the thin film, are found to be identical respectively, to the γ(B_{3}O_{3}) bending mode of planar orthoborate and the asymmetric

Figure 3. IR spectrum. a, (Zinc, bismuth) borate base glass. b, Thin film of a mixture of boron and bismuth complexes of fullerene extracted from the green composite glass.
stretching νas[Br4+O] mode of tetrahedral [BO4] units of the base glass. The appearance of these bands along with the band of B3O–O asymmetric stretching mode in the range 1270–1290 cm⁻¹ in the spectrum of the film, suggests that borate-related species are present in the extract of the complexes. As discussed earlier, only the smaller units of glass like BO3, B4O5, Bi3B2O7, Bi2B4O9, and Bi4B6O15, which are linked to fullerene are likely to migrate in the extract. A bismuth-borate unit is normally known to have at least one tetrahedral borate [BO4] along with planar [BO3] in its structure. For example, in the case of Bi2B4O9 the borate anion is built by one [BO3] tetrahedron and two [BO3] triangles. There are many other examples of such bismuth-borate structure. IR results therefore, support the view that both borate and bismuth-borate units of glass chemically interact with C60 to form different complexes.

The band at 1385 cm⁻¹, which is not found in the IR spectrum of the base glass but appears in the spectrum of the complexes, must be associated with the C60-moiety. Such a band is known to arise in the spectrum, when the C60 molecules suffer a loss in I₃₅ symmetry due to the formation of addition complex or undergo self-polymerization through opening of pyryylene bonds. The opening of a pyrylene bond actually causes softening and a red shift of the 1428 cm⁻¹ C = C T₁₅ band of the molecule to 1385 cm⁻¹. It is also known from previous studies that a loss in I₃₅ symmetry of the C60 molecule as a result of some addition reaction through opening of its pyrylene bond/bonds induces a splitting to its highly degenerate 1182 cm⁻¹ F₁₀ mode. The appearance of two new IR bands at 1070 and 1130 cm⁻¹ and simultaneous non-appearance of the 1182 cm⁻¹ band therefore, suggest that the C60 molecules of the composite had undergone addition reaction through opening of their pyrylene bonds. The 1460 cm⁻¹ band of the spectrum seems to be related to the A₁₃ Raman mode of C60 (1469 cm⁻¹). It had appeared in the spectrum with a red shift, also due to loss of symmetry of the fullerene cage and acquiring of charge. The band at 740 cm⁻¹, which is known to appear frequently in the spectra of various complexes of C60, is associated with the normal C–C vibration of the C60 cage. Simultaneous occurrence of ~ 700 cm⁻¹ out-of-plane bending mode, γ[Br₄O] C of planar orthoborate unit and the 740 cm⁻¹ C–C vibration of the C60 cage, possibly show that C60 can >B–O type of rings are present in the structure of some of these complexes. The proposition of formation of such hetero epoxy rings in these complexes is further supported by the appearance of the strong IR band at 1740 cm⁻¹ in the spectrum. This high-frequency band seems to be a combination band of the 740 cm⁻¹ C–C vibration of the C60 cage and the asymmetric ring stretching of the >B–O ring. The asymmetric ring stretching frequency of the pentagonal ring of compounds like phenyl methylene dioxide is known to occur in the ν-range ~ 950 cm⁻¹. This frequency value will increase, in the case of the present (carbon, boron)-pentagonal ring, because of replacement of one carbon atom of the ring by a relatively lighter and less electronegative boron atom. IR results are thus found to corroborate well with those of absorption and mass spectra.

In a bismuth-borate structure, bismuth atoms are known to form different irregular oxygen coordination polyhedra. For example, in Bi2B4O9 crystal the bismuth atoms remain in sixfold oxygen coordination (BiO3). Three bonds in (BiO3) are short, which actually form BiO3 irregular trigonal pyramid with bismuth atom at the top. The other oxygens are at longer distances. The lone pair of electrons of the cation is known to be located nearly opposite to the short bonds. Bismuth-borate units of the present glass will also have similar bismuth–oxygen pyramid with the respective bismuth atoms at the top carrying the lone pair of electrons on the head. Such configuration actually helps the bismuth atoms of the respective bismuth-borate units to form a complex with C60 through donation of lone pair of electrons. The tentative proposed structures for the complexes are shown in the Table 1. The positions of attachment of different addenda to the C60 moiety in a given structure are not absolute. They are assigned only on the basis of minimal steric hindrance.


12. Tagmatarakis, N. and Prassides, K., Synthesis and characterization of organosilica complexes of fullerene derivatives. In Electronic Properties of Novel Materials, Science and Technology of Molecular Nanostructure (eds Kuzmany, Fink, Mehring and...
RESEARCH COMMUNICATIONS

34. Debnath, R. and Sahoo, R., A synergistic composition for preparation of high concentration fullerene (C60)–glass composite in bulk monolith and their applications as nonlinear optical medium and optical limiter, etc. PCT Patent filing no. PCT/IB03/047, India, USA, UK, Germany and France.


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Pyrolysis of rice husk

Anshu Bharadwaj1,*, Y. Wang2, S. Sridhar2 and V. S. Arunachalam2

1Center for Energy and Environment Studies and
2Department of Material Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Rice husk has proved to be a difficult fuel for gasification and fluidized bed combustion because of the high ash content resulting in carbon conversion inefficiency. We report the results of pyrolysis experiments of individual rice husk particles under controlled atmospheres of the confocal scanning laser microscope followed by SEM observations of the pyrolyzed structure of the particles. The results suggest a preferential shrinkage of the particles in the transverse direction, implying the presence of strong and inert silica layer that retains its structure despite high temperatures. The cellulose and lignin component was preferentially consumed in geometrically arranged pores and channels. The role of silica appears to be more than just a geometric shield and thus complete carbon conversion may not be achievable.

Rice husk is the outer covering of paddy and accounts for 20–25% of its weight1. It is removed during rice milling and is used mainly as fuel for heating in Indian homes and industries. Its heating value of 13–15 MJ/kg1,2 is lower than most woody biomass fuels. However, it is extensively used in rural India because of its widespread availability and relatively low cost. The annual generation of rice husk in India is 18–22 million tons3 and this corresponds to a power generation potential of 1200 MW4. A few rice husk-based power plants with capacities between 1 and 10 MW are already in operation and these are based either on direct combustion or through fluidized bed combustion. Both these routes are beset with technical problems because of the chemical composition of rice husk and its combustion characteristics5.

*For correspondence. (e-mail: anshu@cmu.edu)